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Anodic Stripping Voltammetry and Other Studies of Electrode Processes.

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ANODIC STRIPPING VOLTAMMETRY
AND
OTHER STUDIES OF ELECTRODE PROCESSES

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Gleb Mamantov
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ABSTRACT

Part I

Two methods are developed for the analysis of traces of metals (soluble in mercury) by anodic stripping from a stationary mercury electrode Anodic stripping is carried out either by sudden switching of potential (potential-step method) or by passing a constant current through the cell (current-step method) A theoretical analysis is developed for both methods for conditions of semi-infinite linear diffusion. The following derivations are given equations for current-time, current-potential, and potential-time curves diffusion current and transition time for the stripping process, sensitivity gain. Experimental results are discussed for the anodic stripping of cadmium from a hanging mercury drop, and theory and experiment are compared. Sensitivity gains with respect to voltammetry with stirred solution can be larger than 100. Application to analysis in the range of concentrations as low as 10^{-7} - 10^{-9} molar appears feasible. These two methods are compared with anodic stripping at continuously varying potential (Nikelly and Cooke).

Part II

The following mechanism is proposed for the discharge of negatively charged metallic complexes. (1) Reduction occurs simultaneously (a) by the direct electrochemical reaction of the complex and (b) with chemical transformation $MX_p^{-q} \rightleftharpoons MX_{p-1}^{-(q-1)} + X^-$ prior to reduction. (2) The relative contributions of these two simultaneous processes vary

with potential. Reduction with preceding chemical transformation is predominant at potentials markedly negative with respect to the point of zero charge. Conversely, direct reduction is predominant at potentials somewhat positive with respect to the point of zero charge. There is a progressive transition from one extreme case to the other.

Experimental evidence based on the application of voltammetry at constant current is presented. The conclusions about the mechanism are based on the variation with current density (i_o) of the product of the current density by the square root of the transition time (τ). Chemical transformation prior to discharge corresponds to a linear variation of $i_o\tau^{1/2}$ *vs.* i_o with a negative slope. Conversely, the product $i_o\tau^{1/2}$ is independent of i_o for direct discharge.

Positively charged complex ions which were studied are reduced directly.

FOREWORD

Since this dissertation is divided into two parts which are not directly related, the review of literature and the discussion of experimental methods will be presented separately for each part. Experimental methods are described after the theoretical treatment in Part I because this order of presentation better fits the discussion of material.

PART I

ANODIC STRIPPING VOLTAMMETRY

CHAPTER I

INTRODUCTORY REMARKS AND REVIEW OF LITERATURE

Anodic stripping methods [38] have recently been applied again to the analysis of traces of metals [11, 25, 27]. The metal to be determined in a solution is first deposited on a solid [25, 27] or amalgamated [11] electrode, and then is stripped from this electrode by anodic oxidation. The amount of metal in the solution is determined from the quantity of electricity consumed in the stripping process. Nikelly and Cooke [39] recently modified the method and used a mercury pool electrode for deposition of the metal to be analyzed. They reoxidized the metal at continuously varying potential and obtained current-potential curves not unlike those of oscillographic polarography. These curves exhibit a peak from the height of which the concentration of the metal is directly deduced. The method of Nikelly and Cooke is a voltammetric procedure whereas previous methods belong to coulometry. These authors coined the expression "anodic stripping polarography" for their method, but it would be preferable to call it "anodic stripping voltammetry", thus reserving the term "polarography" for methods involving the use of the dropping mercury electrode [5].

In addition to the method of Nikelly and Cooke, two other simple methods can be devised: (a) the "potential-step" method in which the metal is oxidized by a sudden change of potential to a more anodic value; and (b) the "current-step" method in which the stripping process is carried out at constant current. These methods are discussed and compared in this dissertation for the case of stationary mercury electrodes.

CHAPTER II

POTENTIAL-STEP METHOD

DIFFUSION STRIPPING CURRENT

A metal M is deposited at constant potential on a stationary mercury electrode in stirred solution. The conditions are such that the electrolysis current is constant, i.e., the volume of solution is so large and the plating time so short that depletion of ions M^{+n} in solution can be neglected. Electrolysis is carried out at a potential corresponding to the limiting current range. Mercury is not stirred, and M is supposed to diffuse in the bulk of mercury under conditions of semi-infinite linear diffusion. After τ seconds the potential is abruptly changed to a sufficiently anodic value at which metal M is oxidized at a rate that is solely diffusion controlled. The resulting diffusion stripping current will now be derived. This current is obtained by deriving the flux of metal M at the electrode surface, e.g., by solving Fick's diffusion equation

$$\frac{\partial C_M}{\partial t} = D_M \frac{\partial^2 C_M}{\partial x^2} \qquad (2\text{-}1)$$

C_M - the concentration of the metal M in mercury

x - the distance from the electrode surface in mercury

for the following initial and boundary conditions.

The initial condition expresses the concentration of M in mercury at time τ, i.e., at the instant of switching of potential. This concentration is (21, 5)

$$C_M(x,0) = \frac{i_p}{nFAD_M}\left[2\left(\frac{D_M\tau}{\pi}\right)^{1/2}\exp\left(-\frac{x^2}{4D_M\tau}\right) - x\,\mathrm{erfc}\left(\frac{x}{2D_M^{1/2}\tau^{1/2}}\right)\right] \qquad (2\text{-}2)$$

where i_p is the plating current during deposition of M on mercury, D_M the diffusion coefficient of M in mercury, n the number of electrons for the discharge of M^{+n}, F the faraday, A the electrode area, and "erfc" represents the error function complement. The notation $C_M(x,o)$ is used to indicate that the origin of time in the following derivation is taken at the beginning of the stripping process.

As a boundary condition it is prescribed that M is immediately oxidized to M^{+n} as it reaches the electrode surface. Hence, $C_M(o,t) = 0$ for $t > 0$. Finally, $C_M(x,t) \longrightarrow 0$ for $x \longrightarrow \infty$ and for $t > 0$.

This boundary value problem is quite similar to the one previously studied in this laboratory for two consecutive electrode reactions in voltammetry at constant current [3]. The complete derivation which is given in appendix yields the following result:

$$-\frac{i_{s,d}}{i_p} = \frac{2}{\pi}\left(\frac{\tau}{t}\right)^{1/2} - \frac{1}{2} - \frac{1}{\pi}\sin^{-1}\frac{\tau - t}{\tau + t} \qquad (2\text{-}3)$$

where $i_{s,d}$ is the diffusion stripping current. According to polarographic practice, the anodic current $i_{s,d}$ is negative and the cathodic current i_p is positive in (2-3).

Variations of $-i_{s,d} / i_p$ with t/τ are shown in Fig. 1. Solid curve represents exact solution in equation (2-3); dashed curve corresponds to the approximate solution $-\frac{i_{s,d}}{i_p} = \frac{2}{\pi}\left(\frac{\tau}{t}\right)^{1/2}$. It is seen from this diagram that the ratio $-i_{s,d}/i_p$ is much larger than unity provided that t/τ is sufficiently small. One has $-i_{s,d} / i_p \longrightarrow \infty$ for $t/\tau \longrightarrow 0$ and $-i_{s,d} / i_p \longrightarrow 0$ for $t/\tau \longrightarrow \infty$.

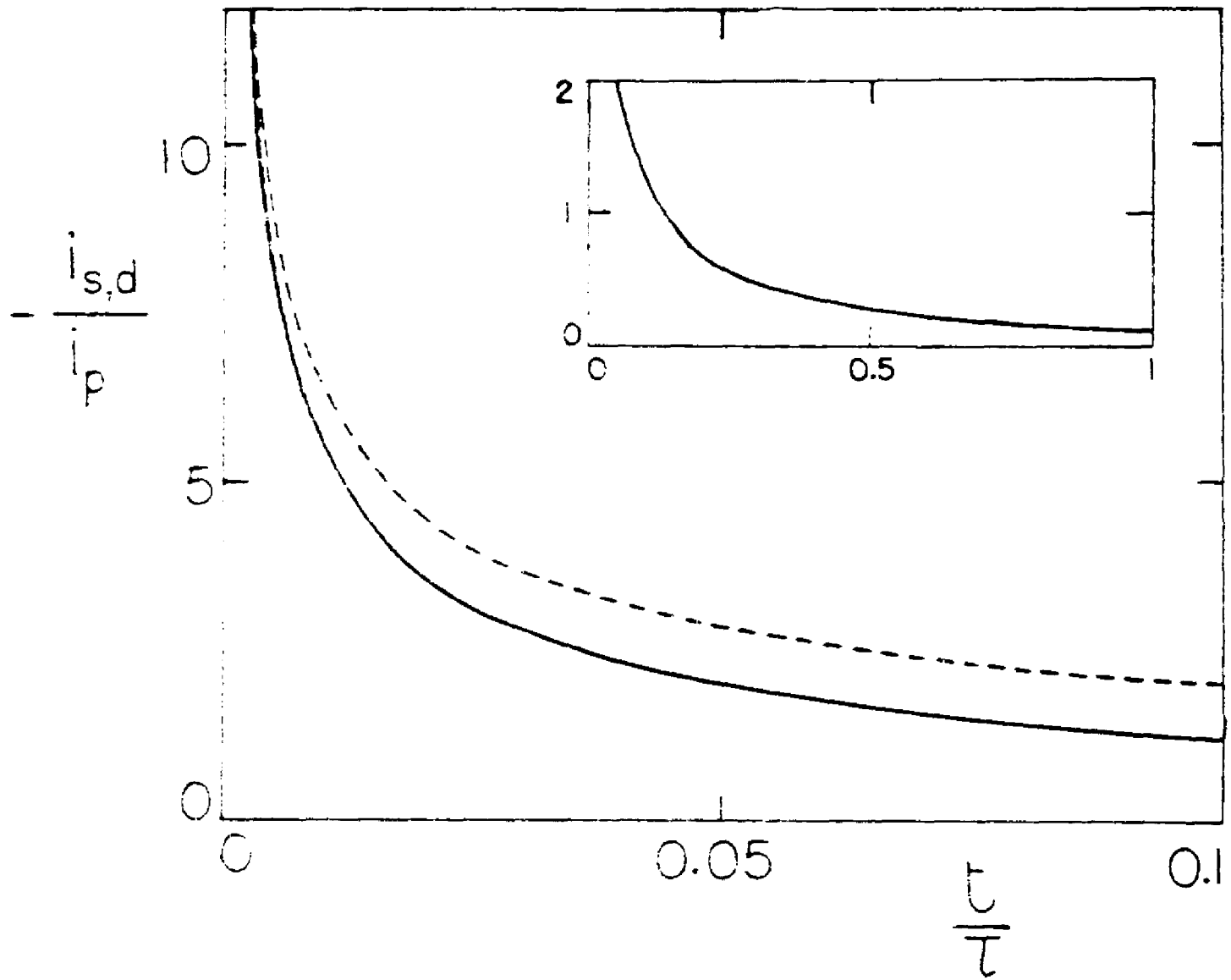

Figure 1

Variations of $-i_{s,d}/i_p$ with t/τ for the Plane Electrode in the Potential-Step Method

Tracings of experimental curves $i_{s,d}$ against t are shown in Fig. 2 for the anodic stripping of cadmium for different pre-electrolysis times. Numbers on curves are pre-electrolysis times in seconds; stripping potential, -0.25 volt (versus S.C.E.). For reasons discussed in the experimental part, these curves were recorded with a hanging mercury drop and not with a mercury pool. Furthermore, the mechanical stirrer was stopped at the end of pre-electrolysis and 4 seconds were allowed to elapse before the recording of the current-time stripping curves. Deformation of the drop during stripping was avoided in this fashion and results were more reliable. These conditions do not correspond to the foregoing theoretical analysis, which should be regarded primarily as a guide for a judicious choice for experimental studies. Note that the experimental curves have the same general shape as the theoretical curve of Fig. 1 (see also below).

The term $(2/\pi)(\tau/t)^{1/2}$ in equation (2-3) is determinative for short and very long times (dashed curve in Fig. 1). This is the ratio $-i_{s,d} / i_p$ one would calculate by assuming that the concentration $C_M(x,o)$ at the instant of switching of potential is independent of x and equal to the concentration at x = o. Thus, one deduces from (2-2) for t = o (i.e., after τ seconds of pre-electrolysis),

$$C_M(0,0) = 2\left(\frac{D_M \tau}{\pi}\right)^{1/2} \frac{i_p}{nFAD_M} \qquad (2\text{-}4)$$

By introducing this concentration in the Ilkovic equation, as written for the plane electrode, there follows the approximate relationship $-i_{s,d} / i_p = (2/\pi)(\tau/t)^{1/2}$. The resulting approximation is quite satisfactory for short times, i.e. for $t/\tau < 0.01$. For larger values of t/τ, the effect of the non-uniform initial concentration distribution is very pronounced (Fig. 1) at least until t/τ is

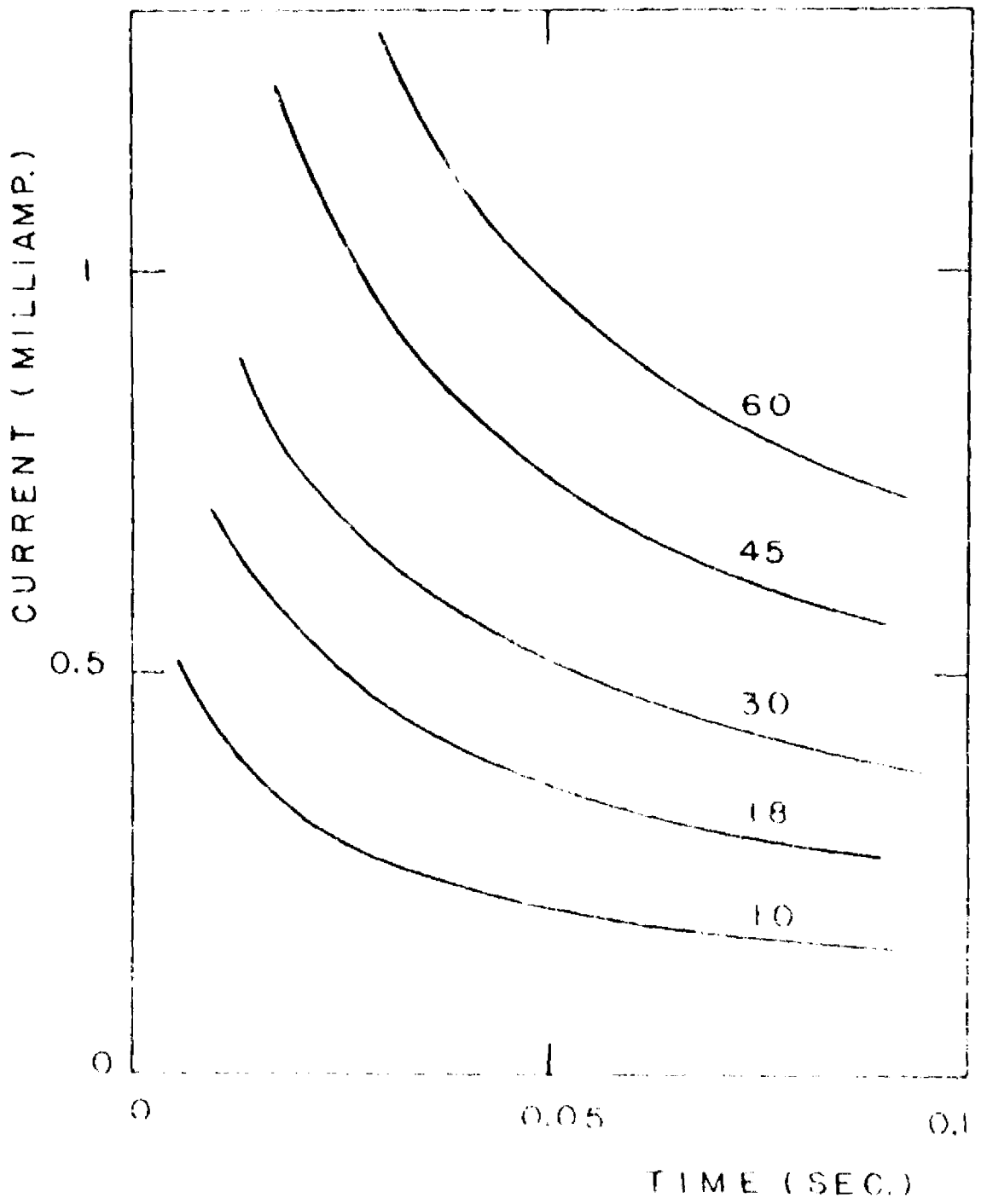

Figure 2

Tracings of Diffusion Stripping Current Time Curves for the Anodic Stripping of Cadmium in 1 M Potassium Chloride

much larger than unity The term $(2/\pi)(\tau/t)^{1/2}$ is again determinative for $t/\tau \gg 1$ because the last two terms in (2-3) cancel the argument of the term in $\sin^{-1}$ is then approximately equal to -1, and $\sin^{-1}(-1) = -\pi/2$.

It follows from these considerations that a plot of $i_{s,d}$ against $1/t^{1/2}$ should be linear for $t/\tau < 0.01$. This is indeed the case (Fig. 3) even for the conditions prevailing in the recording of the curves of Fig. 2 (spherical electrode, time interval between preelectrolysis and anodic stripping). Note that the extrapolated segments of the lines of Fig 3 pass through the origin

It is of interest to calculate the recovery of metal M during stripping. The recovery, which is defined as the ratio $\left[-\int_0^t i_{s,d}\,dt\right] / i_p\tau$, is obtained by integrating $i_{s,d}$ from 0 to t Integration is performed by expanding $\sin^{-1}\left[(\tau - t)/(\tau + t)\right]$ in series[1] and by retaining only the first term. The resulting approximation is fairly good since the argument is practically equal to unity for $t/\tau \ll 1$ and the term in $\sin^{-1}$ is quite unimportant. Variations of the recovery with t/τ are shown in Fig. 4. It is seen from this diagram that the recovery is small (< 10 per cent) for $t/\tau < 0.01$. For long times, the recovery is surprisingly good; it approaches unity for $t/\tau \longrightarrow \infty$

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[1] $\sin^{-1} y = y + \frac{y^3}{6} + \frac{1 \times 3}{2 \times 4} \cdot \frac{y^5}{5} \ldots\ldots$

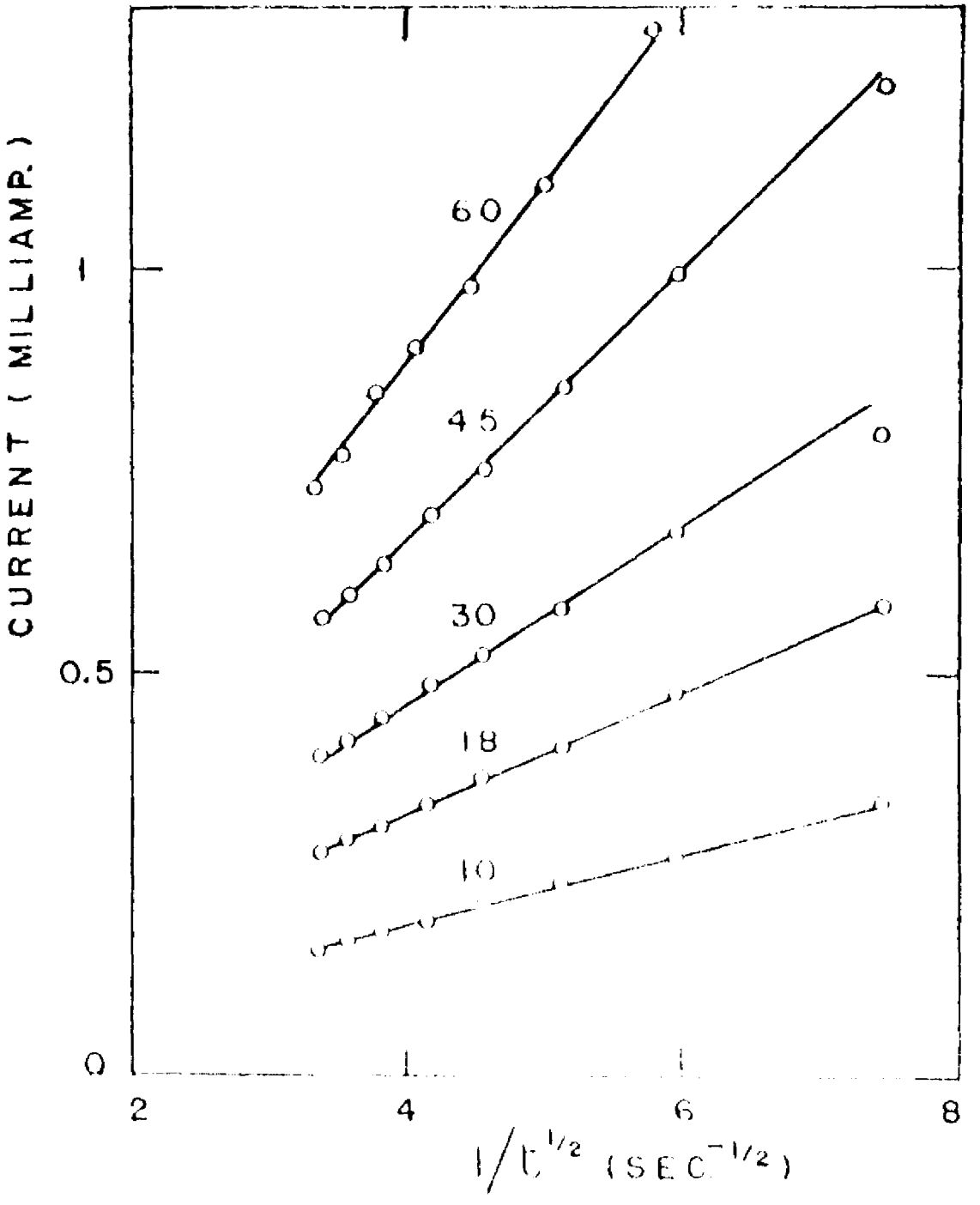
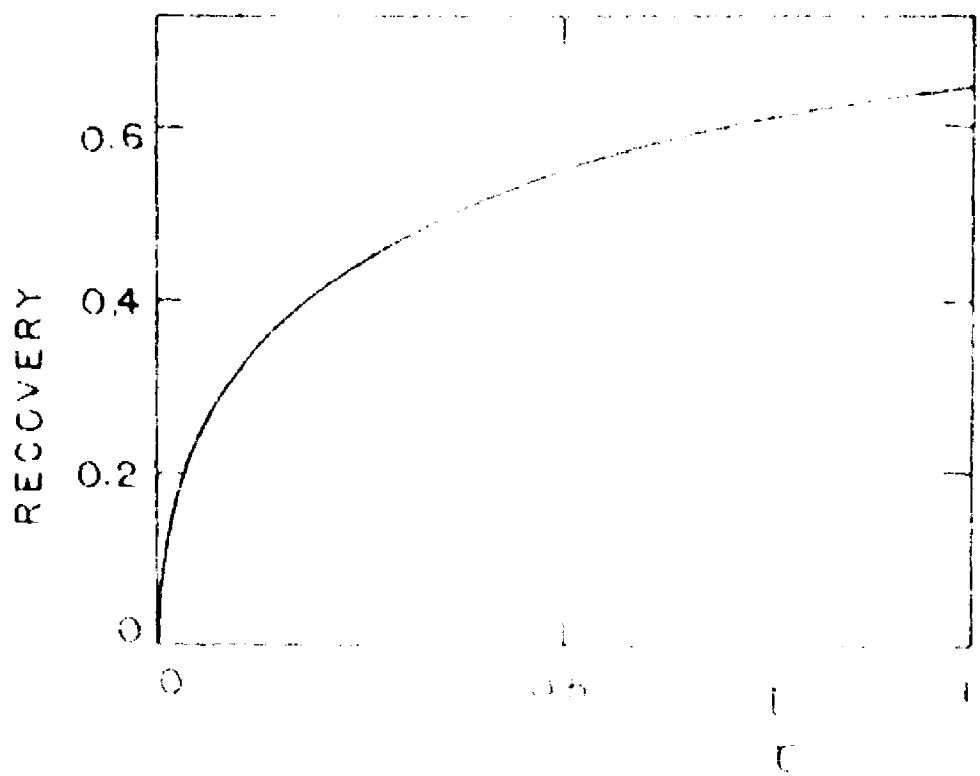


Figure 5

Plot of Diffusion Controlling Current against $1/t^{1/2}$



Recovery as a Function of [illegible]

SENSITIVITY GAIN

The gain in sensitivity can be expressed in two ways, (a) as the ratio $-i_{s,d} / i_p$ of equation 2-3 or (b) as the gain $-i_{s,d} / i_d$ where i_d is the diffusion current measured directly with the analyzed solution (e.g. without pre-electrolysis) and for the same time t as $i_{s,d}$. Both methods will be discussed.

The gain in sensitivity, as expressed by equation (2-3) corresponds to the comparison between the stripping method and voltammetry with a stationary electrode in stirred solution. It follows from the discussion of equation (2-3) that the gain for $t/\tau \ll 1$ is approximately $(2/\sqrt{\pi})(\tau/t)^{1/2}$. The ratio $\tau/t)^{1/2}$ should be as large as possible, but there are two limitations (a) convection interferes with diffusion when τ is too long thus causing unreliability, and (b) the charging (or discharging) of the double layer interferes with the stripping current when t is too short. Obviously, one should have $i_{s,d} \gg i_c$ where i_c is the charging current of the double layer. If one makes the approximate assumption that the differential capacity C of the double layer is constant in the interval ΔV of potential during switching of potential one has $i_c = (\Delta V/R)\exp(-t/RC)$ R being the total resistance of the cell circuit. The condition $i_{s,d} \gg i_c$ becomes (using the simplified form of equation 2-3)

$$\frac{2}{\sqrt{\pi}}\left(\frac{\tau}{t}\right)^{1/2} i_p \gg \frac{\Delta V}{R}\exp\left(-\frac{t}{RC}\right) \qquad (2\text{-}5)$$

If an electrode area of 0.03 cm^2 (see Chapter 4) is utilized C is of the order of 1 microfarad and the time constant RC should be less than 10^{-3} second for a cell having not too high a resistance (R $\leq$ 1000 ohms). For t = 0.01 sec, R = 1000 ohms

ΔV = 0.5 volt, and τ = 100 sec. condition (2-5) becomes $i_p \gg 5 \times 10^{-10}$ amp. This condition is easily fulfilled with an electrode of 0.03 cm^2 even for very dilute solutions. Hence the capacity current could be neglected for $t \geq 0.01$ sec. Actually, there are traces of impurities adsorbed on the electrode, and the switching of potential generally causes a variation in the surface concentration of these impurities. Variations of surface concentrations are quite slow [9], and the capacity current may not die out for times appreciably longer than t = 0.01 sec. In the analysis of traces of metals removal of traces of adsorbable organic substances is recommended, possibly by chromatography [19]. However, experimental gains of the order of 100 are possible. Since voltammetry with stirred solution is applicable to concentrations as low as 10^{-6} - 10^{-7} molar [23-28], application of the potential-step stripping method to solutions even as dilute as 10^{-8} molar appears feasible.

Experimental gains are given in Table I for conditions similar to those of Fig. 2 (hanging mercury drop, 4 second interval between pre-electrolysis and anodic stripping). Gains of the order of 100 were obtained for the longest plating time (180 sec.). Experimental and theoretical gains which are in fairly good agreement for short pre-electrolysis times (τ = 10 sec.) are quite different for the larger values of τ. There are two main reasons for this discrepancy. Firstly, convection of metal M in mercury causes a loss of metal in the layer adjacent to the mercury surface, and this tends to decrease the gain. Conversely, diffusion of M in a small mercury sphere (perhaps 1 mm. in diameter) is slower than for semi-infinite linear diffusion and metal M diffuses away from the mercury surface more slowly in a hanging mercury drop than in a mercury pool.

TABLE 1

EXPERIMENTAL GAIN FOR HANGING MERCURY DROP VERSUS CALCULATED GAIN FOR A PLANE ELECTRODE -- ANODIC STRIPPING OF CADMIUM

τ	$\tau^{1/2}$	$i_{s,d}$[2]	$i_{s,d} / i_p$	$i_{s,p} / i_p$
sec.	10^{-2} sec.	mA	experimental	calculated
180	3	4.62	136	48.4
180	6	3.18	93.5	34
180	9	2.49	73	27.5
60	3	1.29	59	27.5
60	6	0.90	35	19.1
60	9	0.73	28	15.5
30	2.8	0.68	26	13.8
30	5.8	0.49	18.8	13.3
30	8.8	0.40	15.4	11.8
10	2.8	0.274	10.5	11.7
10	5.8	0.196	7.54	7.4
10	8.8	0.160	6.16	5.8

[2]The pre-electrolysis current was 26 microamp. except for τ = 180 sec. for which it was 34 microamp.

This results in an increase in gain which becomes more pronounced as τ is made larger. It is seen from Table I that the effect of the sphericity of the electrode outweighs the influence of convection. The theoretical analysis of the stripping method for the hanging mercury drop is more involved than for mercury pool, it will not be discussed here.

The second method of expressing the sensitivity gain is to compare $i_{s,d}$ with the diffusion current i_d measured at time τ in direct voltammetry without pre-electrolysis. The current i_d is given by the Ilkovic equation written for the plane electrode. The gain calculated by the simplified form of equation 2-3) and by replacing i_p by its value $i_p = nFAD_{M+n} C^0 / \delta$ (C^0 bulk concentration of M^{+n}, δ diffusion layer thickness), is $(2/\pi)^{1/2} D^{1/2} \tau^{1/2} / \delta$.

One has $i_{s,d} / i_d \approx 40$ for data of the following orders of magnitude: $D = 10^{-5}$ $cm^2 sec^{-1}$, $\tau = 100$ sec, and $\delta = 10^{-3}$ cm. (an approximate value of the conditions in the experimental study[3]). The anodic stripping method is thus more sensitive than the direct method. Actually, we found that direct voltammetry is not satisfactory at low concentrations (below 10^{-5} molar) because of interference by adsorbed impurities on the electrode (oxide film on mercury). This difficulty is greatly minimized in stripping voltammetry because of pre-electrolysis.

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[3]Data were: $i_p \approx 3 \times 10^{-5}$ amp, $n = 2$, $A \approx 3 \times 10^{-2}$ cm^2, $D = 10^{-5}$ $cm^2 sec^{-1}$, $C^0 = 5 \times 10^{-7}$ mole cm^{-3}.

CURRENT-POTENTIAL CURVES

The potential after pre-electrolysis is now switched to a value at which the concentration of metal M at the electrode surface is larger than zero during stripping. A set of current-time curves[4] (Fig. 5) is obtained for different stripping potentials. Numbers on curves are stripping potentials in volts *versus* S.C.E.). Pre-electrolysis time, 10 seconds; time interval between pre-electrolysis and stripping, 4 seconds. By measuring the current on each of these curves at a given time, one can construct a current-potential curve for that particular stripping time. These curves will now be discussed on the assumption that the Nernst equation is applicable. It first will be assumed that the solution is stirred during stripping and that there is no time interval between pre-electrolysis and stripping.

To derive the equation of the i_s *versus* t curves for any potential we could use again the initial condition (2-2) for M and prescribe that the ratio $C_{M^{+n}} / C_M$ at x = o is equal to a constant readily given by the Nernst equation. Another boundary condition would be obtained by prescribing that the sum of the fluxes of M and M^{+n} at x = o is equal to zero. The approach is the same as in the rigorous derivation of reversible polarographic waves (5), but the algebra is far more involved -- in fact, too involved for the result to be achieved. It is much easier to assume that C_M is independent of x at t = o and has the value given by equation (2-4). This approximation is very good for $t / \tau \leq 0.01$ (see

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[4]Note that the curves for -0.90, -0.80, and -0.70 volt in Fig. 5 correspond to the limiting current range for pre-electrolysis. The current decreases progressively because of concentration polarization. Thus, the electrolysis circuit was open after pre-electrolysis and closed again after the interval of 4 seconds, the solution being not stirred after pre-electrolysis.

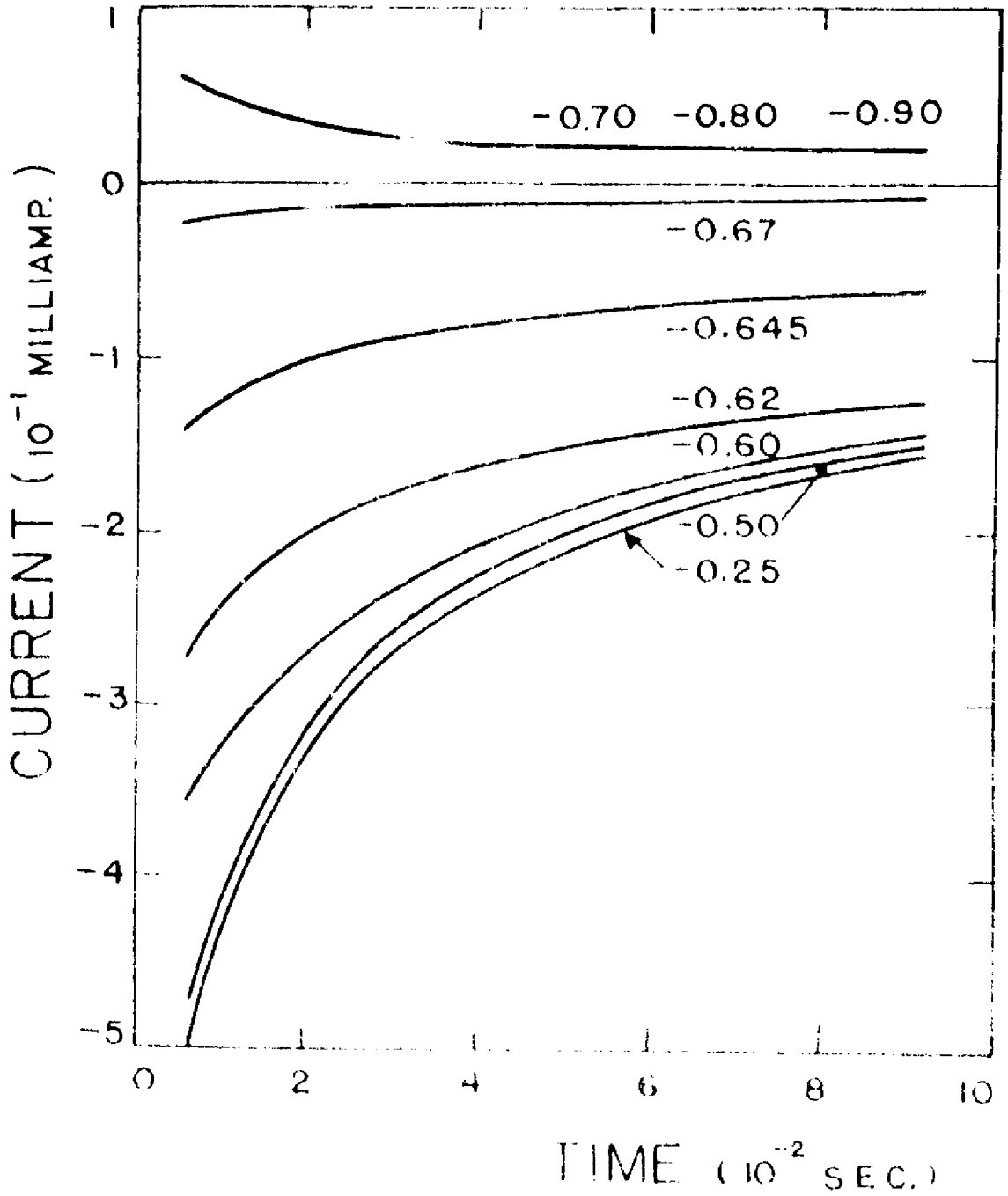

Figure 5

Traces of Current-Time Curves for the Anodic Stripping of Copper from a Platinum Electrode

above) but is poor for $t/\tau > 0.1$ The concentrations $C_{M^{+n}}(o,t)$ and $C_M(o,t)$ are calculated as follows

The concentration $C_{M^{+n}}(o,t)$ during stripping is deduced from the condition that the sum of the fluxes of M and M^{+n} at $x = o$ is equal to zero. On the basis of the Nernst diffusion layer treatment, the flux of M^{+n} during stripping which is equal to i_s / nFA is $D_{M^{+n}} \left[C_{M^{+n}}(o,t) - C^{\circ} \right] \delta$. δ being the diffusion layer thickness, and C° the bulk concentration of M^{+n}. The thickness δ can be evaluated from $i_p = nFA\, D_{M^{+n}}\, C^{\circ} / \delta$ Hence

$$C_{M^{+n}}(0,t) = C^{\circ}\left[1 - \frac{i_s}{i_p}\right] \qquad (2\text{-}6)$$

The concentration $C_M(o,t)$ is derived by noting that, as in polarography theory, i_s is proportional to the difference $\left[C_M(o,o) - C_M(o,t) \right]$, the proportionality factor being deduced from the Ilkovic equation written for the plane electrode By using for $C_M(o,o)$ the value given in (2-4) there follows after simple transformations

$$C_M(0,t) = C_M(0,0)\left[1 - \frac{i_s}{i_{s,d}}\right] \qquad (2\text{-}7)$$

By introducing the C's from (2-6) and (2-7) in the Nernst equation one obtains after rearrangement of terms

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{f_{M^{+n}}}{f_M} \frac{nFAD_M^{1/2}C^{\circ}}{\pi^{1/2} i_p} \cdot \frac{1}{t^{1/2}} - \frac{RT}{nF} \ln \frac{i_s - i_{s,d}}{i_p - i_s} \qquad (2\text{-}8)$$

As in the foregoing treatment, anodic stripping currents are negative in equations (2-6) to (2-8), and the cathodic current i_p is positive. The half-wave potential, which is equal to the sum of the

first two terms on the right-hand side of (2-8) is shifted toward less anodic potentials as the time t increases. The half-wave potential corresponds to $i_s = i_{s,d} + i_p/2$ and is the point of inflection of the current-potential curve (set $d^2E/di^2 = 0$). The potential at i = 0 is independent of time. Its value is obtained by setting $i_s = 0$ in (2-8) and by noting that $-i_{s,d} = i_p$ is set equal to $(2/\pi)(\tau/t)^{1/2}$ in this simplified treatment.

Equation (2-8) still holds as a simplified formula for the case in which stirring is stopped after pre-electrolysis and a time interval elapses before anodic stripping, but the half-wave potential has now the value $E^0 + (RT/nF)\ln f_{M^{n+}} - f_M(D_M/D_{M^{n+}})^{1/2}$ and is independent of time. This is the value derived in the theory of reversible polarographic waves.

Current-potential curves deduced from the data of Fig. 5 are plotted in Fig. 6 for different values of t. Numbers on curves are the times in seconds at which current was measured. The half-wave potential is independent of time and has the same value (-0.64 volt versus S.C.E.) as the polarographic half wave potential. The foregoing approximate analysis is thus quite satisfactory for the stripping times involved here.

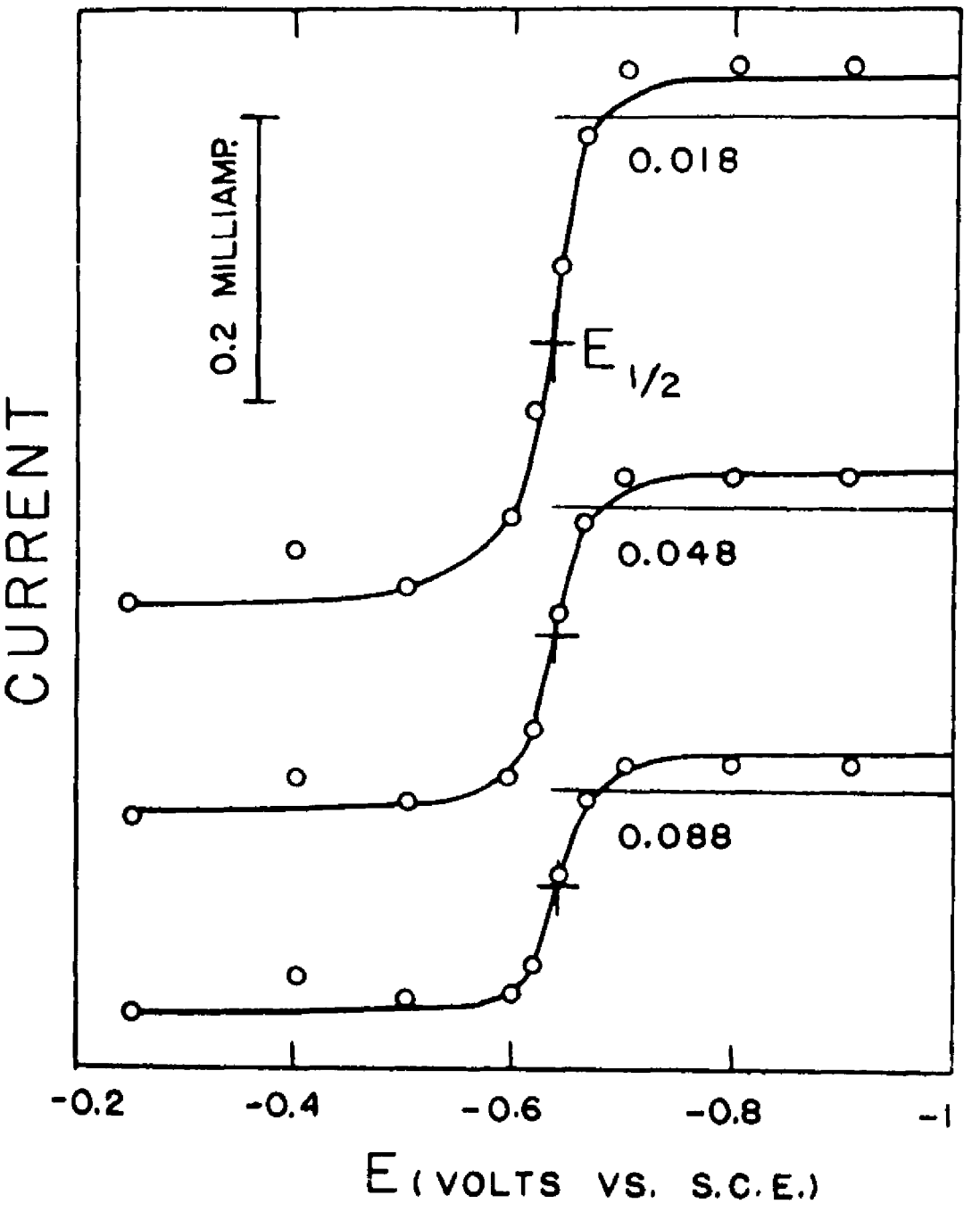

Figure 6

Current-Potential Curves from the Data of Figure 5

CHAPTER III

CURRENT-STEP METHOD

TRANSITION TIME AND SENSITIVITY GAIN

The conditions are the same as in the potential-step method except that anodic stripping is carried out at constant current. The potential of the amalgam electrode is followed during anodic stripping, and a potential-time curve is recorded. This curve exhibits a rapid variation of potential at the transition time τ_s i.e. at the time at which C_M o τ_s). Experimental potential-time curves are given in Figure 7. Numbers on curves are pre-electrolysis times in seconds. Stripping current density 1.56× 10^{-3} amp cm^{-2} Time interval between pre-electrolysis and stripping, 4 seconds. The ratio, τ_s / τ , of the transition time τ_s to the pre-electrolysis time τ , was calculated by Berzins and Delahay [2]

$$\frac{\tau_s}{\tau} = \frac{1}{\left(1 - \frac{i_s}{i_p}\right)^2 - 1} \qquad (3\text{-}1)$$

with i_p positive and i_s negative. Experimental and calculated values of τ_s / τ are compared in Table 1. for the anodic stripping of cadmium from a hanging amalgam drop. The agreement is relatively good in view of the two sources of discrepancy sphericity of the electrode and loss of metal in mercury by corrosion. The effect of sphericity becomes more pronounced as the electrolysis is prolonged (compare data for τ = 10 sec. and τ = 75 sec.)

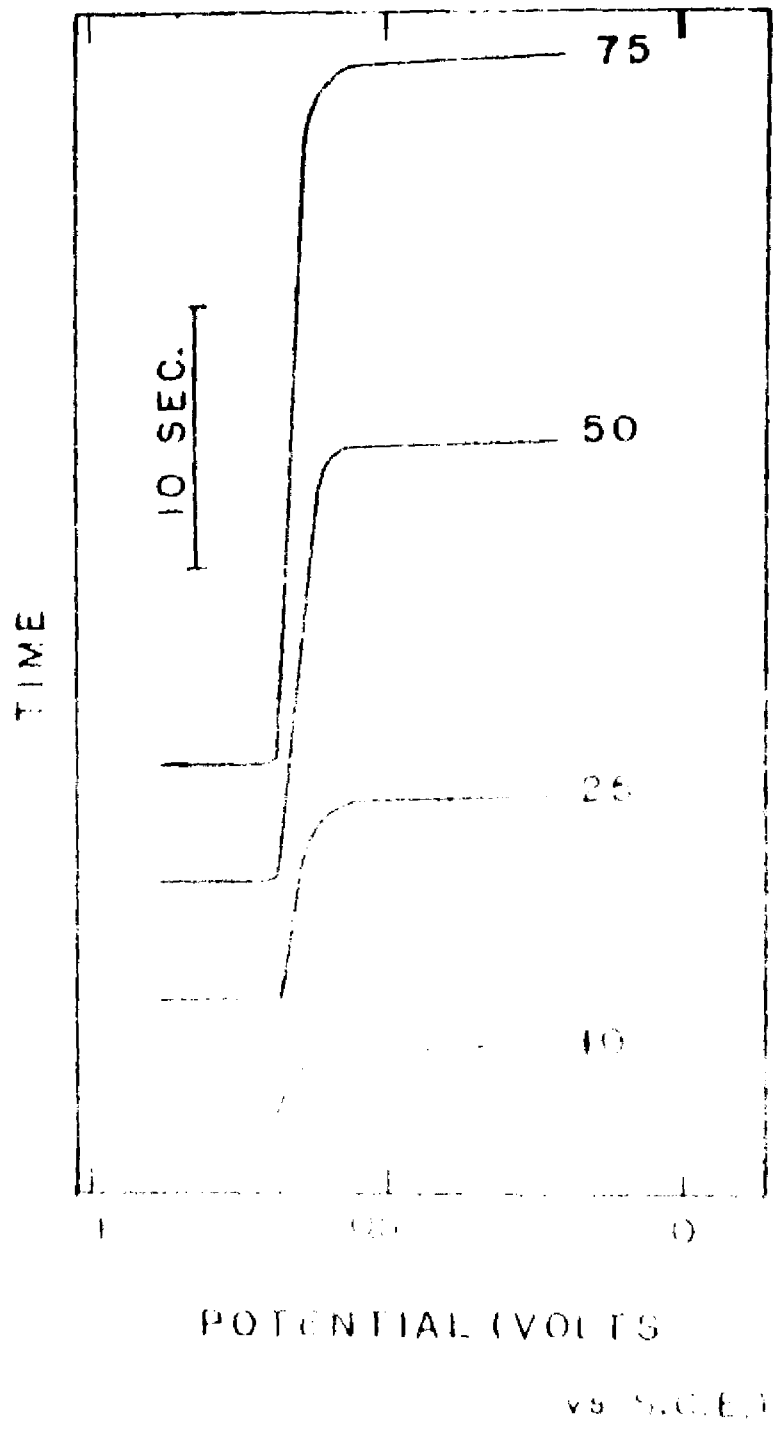
75
50
25
10
10 SEC.
TIME
POTENTIAL (VOLTS

TABLE II

EXPERIMENTAL RATIO τ_s / τ FOR HANGING MERCURY DROP VERSUS CALCULATED GAIN FOR A PLANE ELECTRODE -- ANODIC STRIPPING OF CADMIUM

i_s[1] microamp.	τ sec.	τ_s sec.	τ_s / τ experimental	τ_s / τ calculated
9.9	10	17.5	1.75	2.18
19.6	10	8.5	0.85	1.02
49.4	10	2.4	0.24	0.32
49.4	25	7.8	0.31	0.32
49.4	50	16.0	0.32	0.32
49.4	75	27.2	0.36	0.32

[1]Pre-electrolysis current, 48 microamperes; electrode area, 3.16×10^{-2} cm.^{2}

The sensitivity gain can be expressed by comparing τ_s with the transition time τ_d that would be observed in direct electrolysis at current i_s without pre-electrolysis. Since $\tau_d^{1/2}$ is proportional to the bulk concentration of reducible substance the ratio $(\tau_s / \tau_d)^{1/2}$ and not $\tau_s - \tau_d$ should be considered to express the gain in sensitivity. The gain is $(\tau / \tau_d)^{1/2} \left[(1 - i_s / i_p)^2 - 1 \right]^{-1/2}$. For the data of Table I (τ = 10 sec, τ_s = 17.5 sec.), one evaluates a gain of $(\tau_s - \tau_d)^{1/2}$ of approximately 6 over the direct method[2]. Actually the direct method is not easily applied at low concentrations (adsorbed impurities capacity effects) and the stripping method is more advantageous than this simple calculation of the gain would indicate.

POTENTIAL-TIME CURVES

As in the potential-step method we consider only the case in which the Nernst equation is applicable. By introducing the value of the concentration derived by Berzins and Delahay (2)

$$C_M(0,t) = \frac{2\left[i_p(\tau+t)^{1/2} - (i_p - i_s)\,t^{1/2}\right]}{\pi^{1/2} n F A D_M^{1/2}} \qquad (3\text{-}2)$$

and $C_{M^{+n}}(0,t)$ from equation (2-6) the Nernst equation then follows after simple transformations

$$E = E^\circ + \frac{RT}{nF} \ln \frac{f_{M^{+n}}}{f_M} \cdot \frac{\pi^{1/2} n F A D_M^{1/2} C^\circ}{2 i_p} - \frac{RT}{nF} \ln \left[(\tau+t)^{1/2} \frac{i_p}{i_p - i_s} - t^{1/2} \right] \qquad (3\text{-}3)$$

---

[2] On the basis of the evaluated value $\tau_d \approx$ 2.5 sec.

The potential becomes progressively more anodic as the electrolysis proceeds (Fig. 7). The potential at t = o is readily deduced from (3-3); it depends on pre-electrolysis time and current. It follows from (3-3) that a plot of log $\left[(\tau + t)^{1/2} \frac{i_p}{i_p - i_s} - t^{1/2} \right]$ against E should have the reciprocal slope 0.059/n at 25°. This is essentially the case for the curves of Fig. 7 as far as the accuracy of the recording allows this verification.

CHAPTER IV

EXPERIMENTAL METHODS

A cell with hanging mercury drop (13) of the type previously used in this laboratory (1, 37) (Fig. 8) was utilized. A mercury drop falling from a conventional dropping mercury electrode was caught in a small glass spoon and then hung (by rotation of the spoon) on a small gold-plated platinum wire (perhaps 0.1 mm long) sealed in a glass tube with fine tip. The cell was also provided with a constant speed stirrer of the propeller type. The blades of the propeller were below the tip of the dropping mercury electrode and the hanging drop to avoid the projection of mercury drops on the hanging drop. The stopper was made of plastic and was carefully machined to fit the ground glass collar of the cell. Accuracy in the spacing of the electrodes and spoon was far more easily achieved with a plastic stopper than with a ground glass stopper. A saturated calomel electrode was prepared in the other arm of the cell, and the cell had the usual nitrogen inlet.

It was found that the solution could be rather vigorously stirred without dislodging the hanging drop and pre-electrolysis limiting currents were relatively large (diffusion layer thickness of the order of 10^{-3} cm.). Because of vigorous stirring, the pre-electrolysis current dropped within 1-2 seconds to an average constant value after the beginning of electrolysis. The area of the hanging drop was reproducible with an error smaller than 1 per cent (a conservative estimate) in a given

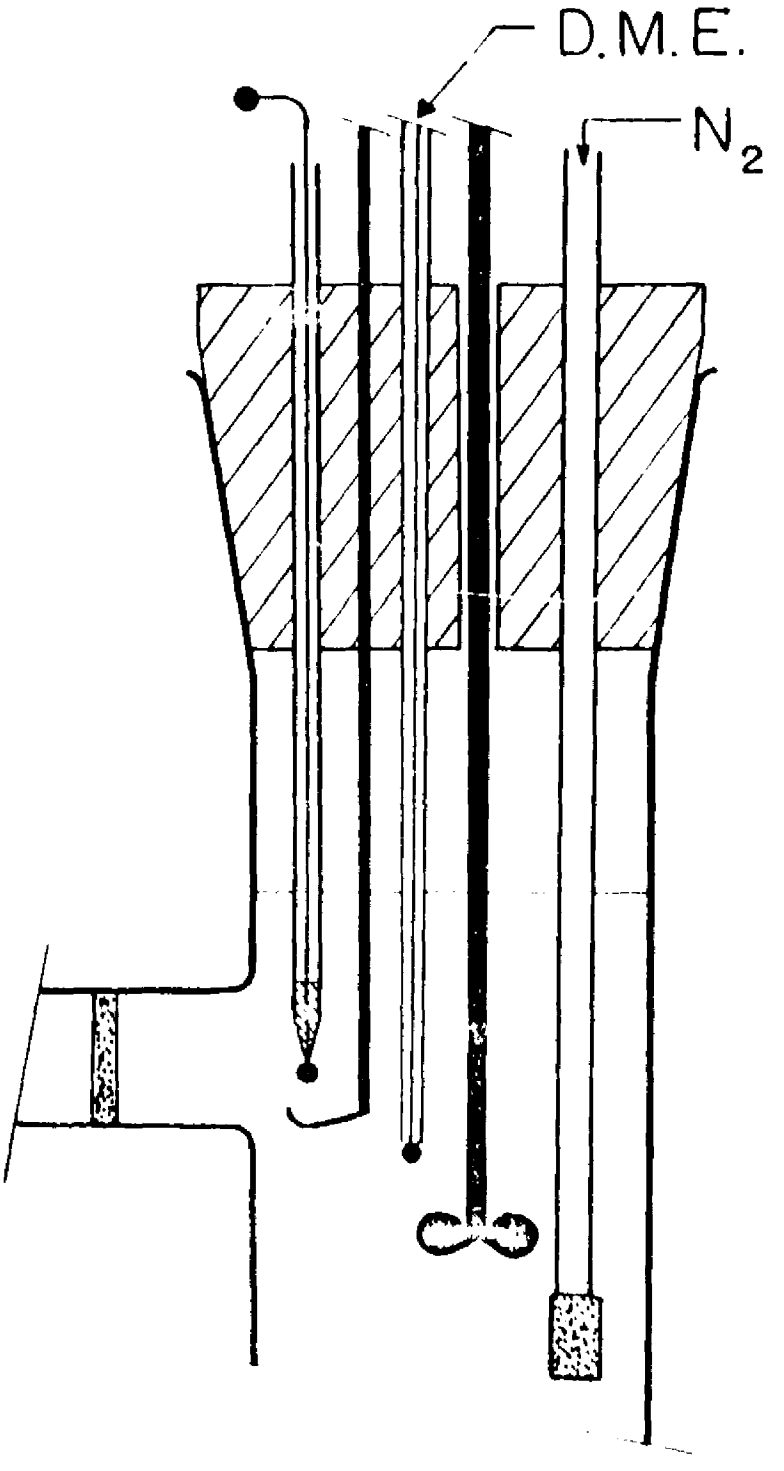

Figure 8

Cell with Hanging Mercury Drop

medium.[1]

Stirring with the rotated propeller stirrer was not uniform and rapid fluctuations of the pre-electrolysis current about a constant average value were observed. The nonuniform stirring also caused deformation of the hanging drop and consequently the stirrer was stopped at the end of pre-electrolysis. A time interval of 4 seconds was allowed to elapse before anodic stripping. The small loss in sensitivity gain was more than compensated by improvement in accuracy.

A cell in which the hanging drop was suspended on a rotating glass tube with gold-plated platinum tip was also used but was not studied in detail. This type of electrode might well be more advantageous than the combination of hanging drop and stirrer.

Instrumentation for the control of the potential of the hanging drop and the stripping current (current-step method) was conventional. Pre-electrolysis was carried out at -1 volt (*versus* S.C.E.) in all the experiments. Time intervals during pre-electrolysis and between stripping and pre-electrolysis were controlled manually with an electric timer. The utilization of time relays would be advantageous and would require only simple instrumentation. Recordings were made with a Tektronix cathode-ray oscilloscope, model 531 with preamplifier 53D.

Solution composition: 0.5 millimolar Cd^{++} in 1M potassium chloride, oxygen removal by nitrogen. The temperature was approximately 25°, it did not vary by more than 1-2 degrees in a series of determinations.

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[1]The reproducibility would be improved by polarizing the dropping mercury electrode at a constant potential just so cathodic as to cause any appreciable metal deposition instead of letting the electrode acquire the mixed potential corresponding to the condition that the algebraic sum of faradaic and capacity currents is equal to zero.

CHAPTER V

CONCLUSION

The two methods studied in this dissertation and the method of Nikelly and Cooke (29) (anodic stripping with continuously varying potential) are of interest in the analysis of traces of amalgam forming metals in the concentration range in which direct voltammetry and polarography fail. Hence, anodic stripping methods have a practical value for concentrations below 10^{-6} molar (6). The sensitivity gain that is achieved results from concentration of the metal to be analyzed in a thin layer at the surface of the mercury electrode. Rather high gains are possible because the metal is deposited in stirred solution at a much higher rate than it diffuses into the bulk of mercury. In this respect, anodic stripping methods can be compared to extraction (10, 18). It should be emphasized that the gain does not result so much from an increase in current to be measured per se (very low currents are quite easy to measure) but rather from an enhancement of current under conditions in which the capacity current is not particularly increased.

A comparison of the gains obtained by the three anodic stripping methods would require actual application to trace analysis, and only the tentative conclusion that the potential-step method is the most sensitive will be made here.[1]

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[1]The sensitivity gain of the method of Nikelly and Cooke can be evaluated by noting that the Randles-Sevcik treatment of oscillographic polarography is applicable as a first approximation when the stirrer is stopped before anodic stripping.

An obvious application of anodic stripping methods would be amperometric titrations at concentrations below 10^{-6} molar.

PART II

MECHANISM OF THE DISCHARGE OF CERTAIN METAL COMPLEXES

CHAPTER VI

INTRODUCTION AND REVIEW OF LITERATURE

The mechanism of the electrochemical reduction of complex ions has been a subject of interest for some fifty years, primarily because of the importance of complex ions in electrodeposition. Parry and Lyons (30) discuss possible mechanisms of reduction of coordination compounds in electroplating, mainly from the historical viewpoint.

It was shown recently by Gierst and Juliard (15) and Delahay and Berzins (7) that certain complex ions are directly reduced, while other complex ions must undergo some chemical reaction before the electrochemical reaction. The same view is shared by Gerischer (14) who studied, in particular, the reduction of cadmium cyanide complexes.

A rather detailed study of complexes had also been made by the writer in 1953-1954 in order to establish a correlation between some properties of complexes and the occurrence of a chemical reaction prior to the electrochemical reaction. No conclusion could be reached at the time. More recently it appeared that negative ions, particularly with a double or triple charge, undergo a chemical transformation before electrochemical reduction. In order to test this hypothesis, the reduction of several negatively charged complexes was studied in the hope that these results together with the results previously obtained would allow to draw definite conclusions regarding the mechanism of reduction of complex ions.

The method used for this investigation was voltammetry at constant

current. Only a brief survey of the theory of constant current will be presented here, since reviews are available (5, 8).

In voltammetry at constant current the electrolysis current is kept constant, and the potential of the polarized electrode is recorded. The solution is unstirred and enough supporting electrolyte is present so that migration of the reducible ion can be neglected. The duration of electrolysis is short — in the present study 0.1 second or less — so that convection can be neglected. Diffusion is thus the only mode of mass transfer.

The experimentally obtained potential-time curves are characterized by a transition time τ whose value was derived by Sand (34). The transition time in the case of linear diffusion without kinetic complications is

$$\tau^{1/2} = \frac{\pi^{1/2} n F D^{1/2} C^{\circ}}{2 i_{o}} \qquad (6\text{-}1)$$

where C° is the bulk concentration of the electrolyzed species, i_{o} the current density, n the number of electrons involved in the reaction, D the diffusion coefficient, and F the faraday. The transition time is defined by the condition that, at $t = \tau$, the concentration of the electrolyzed species at electrode surface is equal to zero. Before the transition time, the potential of the working electrode varies slowly once the decomposition potential for the electrolyzed species has been reached. At $t = \tau$ the potential of the polarized electrode varies rapidly toward more cathodic or anodic values until some new electrode process takes place. The properties of the transition time can be deduced from equation (6-1). Thus, $\tau^{1/2}$ is proportional to the concentration of reducible species and inversely proportional to the current density.

In this study we will be concerned with processes in which electron transfer is preceded by a chemical reaction. In the case of a chemical

reaction of the first order represented by the symbolic equation

$$Z \rightleftharpoons O + ne = R \ ,$$

the transition time τ_k obeys the relationship (7)

$$i_o \tau_k^{1/2} = \frac{\pi^{1/2} nFC^\circ D^{1/2}}{2} - \frac{\pi^{1/2} i_o}{2K(k_f + k_b)^{1/2}} \times \operatorname{erf}\left[(k_f + k_b)^{1/2} \tau_k^{1/2}\right] \qquad (6\text{-}2)$$

where K is the equilibrium constant for the chemical process preceding electron transfer, and k_f and k_b are formal rate constants for this process.

If the current density is sufficiently low, τ_k is relatively large, and the argument of the error function in (6-2) is larger than 2; i.e. the error function is equal to unity. The product $i_o \tau_k^{1/2}$ is then a linear function of the current density. The slope of $i_o \tau_k^{1/2}$ vs. i_o is equal to

$$-\frac{\pi^{1/2}}{2K(k_f + k_b)^{1/2}}$$

If the current density is sufficiently high, it can be shown that equation (6-2) reduces to

$$i_o \tau_k^{1/2} = \frac{\pi^{1/2}}{2} \cdot \frac{nFC^\circ D^{1/2}}{1 + 1/K} \qquad (6\text{-}3)$$

Under these conditions the quantity $i_o \tau_k^{1/2}$ is independent of the current density.

The treatment for reduction preceded by a first order chemical reaction can be extended to a second order process of the type (pseudo-first order)

$$Z \rightleftharpoons O + X$$
$$O \xrightarrow{ne} R$$

provided the concentration of X is sufficiently high (~ 100 times that of Z). It is also assumed that X is neither reduced nor oxidized at the potential at which substance O is reduced.

The slope of $i_o \tau^{1/2}$ vs. i_o then becomes

$$- \frac{\pi^{1/2}}{2} \frac{(C_x^o)^{1/2}}{K' (k_b')^{1/2}}$$

where C_x^o is the bulk concentration of substance X (in our case, the complexing agent), K' is the equilibrium constant for the process $Z \rightleftharpoons O + X$ and k_b' is the rate constant for the backward process Thus the slope of $i_o \tau^{1/2}$ vs. i_o should increase with the concentration of the complexing agent.

CHAPTER VII

EXPERIMENTAL METHODS

The Electrolytic Cell

A conventional H-type cell with a dropping mercury electrode as working electrode was used. The recording was synchronized with the fall of the drop to achieve the same current density for consecutive drops. A rotating contact driven by a synchronous motor (12 rpm) actuated a magnetic hammer which dislodged the mercury drop. Another contact driven by the same motor closed several seconds after the fall of the preceding drop and closed the electrolysis circuit through a mercury relay.

The potential of the dropping mercury electrode was measured against a saturated calomel electrode. The error resulting from the ohmic drop in the cell was greatly reduced by the use of a reference calomel electrode which was inserted in a tube whose drawn out end was within one or two millimeters of the surface of the mercury drop. The second electrode of the electrolysis circuit was an auxiliary platinum electrode inserted in the other compartment of the H-cell. The same solution was used in both compartments.

The solution was freed of oxygen by passing nitrogen through it for 15 minutes. The gas was also passed through the cell before each measurement to eliminate any gradient of concentration.

The Electrolysis Circuit

The circuit utilized is shown in Figure 9. The current was adjusted with the variable resistance R_1 and the current intensity was determined

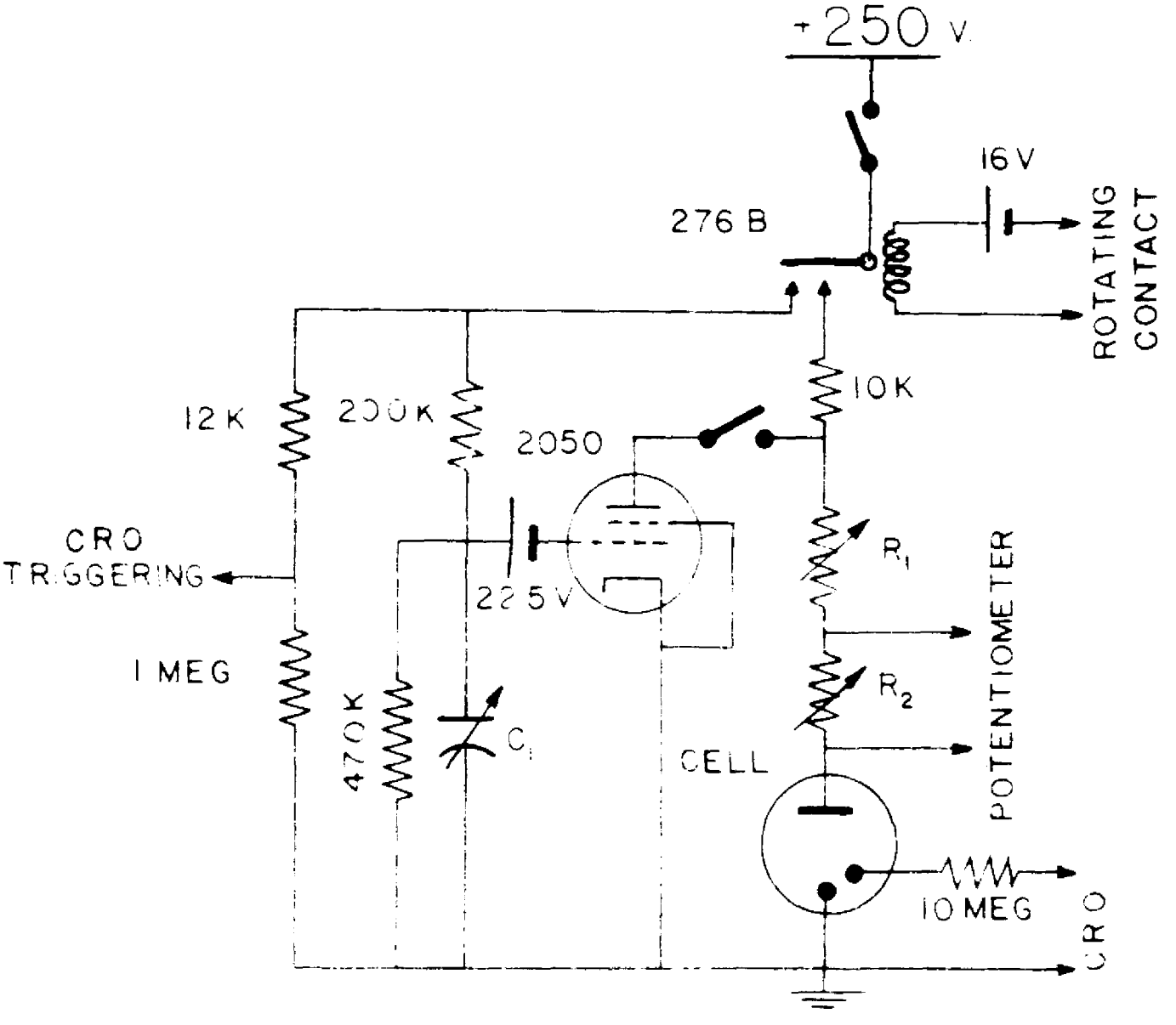

Figure 9

Schematic Circuit Diagram for Voltammetry at Constant Current

by measuring with a Leeds and Northrup student[1] potentiometer the ohmic drop across R_2, a precision decade resistance box. The electrolysis circuit was closed by the mercury relay (Western Electric 276B). This relay is much better than a conventional relay because transients are reduced to a few microseconds. It was indeed necessary to avoid transients particularly in the determination of transition times shorter than a millisecond.

The electrolysis was interrupted before secondary electrode reactions (plating of the supporting electrolyte) could occur to avoid plugging of the capillary of the dropping mercury electrode by potassium or sodium amalgam (supporting electrolytes were prepared with salts of these metals). This was accomplished by connecting a biased thyratron in parallel with R_1 and the cell. After a definite time interval, which was determined by a constant resistance of 200 K and the variable capacitor C_1, the thyratron became conductive, thus short-circuiting R_1 and the cell.

Potential-time curves were recorded with a cathode-ray oscilloscope (Tektronix oscilloscope, model 531 with preamplifier 53D). The oscillograms were photographed on 35 mm film and readings were made from enlarged images.

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[1]This expression is generally used to designate a potentiometer of the type (Catalog No. 7651) manufactured by Leeds and Northrup.

CHAPTER VIII

DESCRIPTION AND DISCUSSION OF EXPERIMENTAL RESULTS

Influence of Charge of Complex on the Mechanism of Discharge

It was pointed out in Chapter VI that at low current densities the product $i_o\tau^{1/2}$ for the discharge of a metallic complex should decrease linearly with the current density if the electrochemical step is preceded by dissociation of the complex provided that this reaction is of pseudo-first order. This was found to be the case for several negatively charged complex ions. The plots of $i\tau^{1/2}$ vs i[1] for these complexes are given in Figures 10 and 11. It is known (22, 20, 17, 8, 24) that all these complexes have a double negative charge, except ferric oxalate which has a triple negative charge. These double and triple negative complexes probably dissociate to the complex with one less negative charge prior to the reduction. Conversely, the product $i\tau^{1/2}$ is independent of current density for positively charged complex ions (Figure 12). In principle, there could be a chemical step prior to reduction; however, the rate constants calculated from a nearly horizontal slope of the plot $i\tau^{1/2}$ vs. i are much higher than those predicted by the absolute rate or collision theories (7).

The effect of concentration of the complexing agent is shown in Figure 13. As was pointed out before, for a pseudo-first order dissociation

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[1]Currents (i) rather than current densities (i_o) are used in Figures 10, 11, and 12. This is permissible since a plot of $i\tau^{1/2}$ vs. i has the same slope as a plot of $i_o\tau^{1/2}$ vs i_o

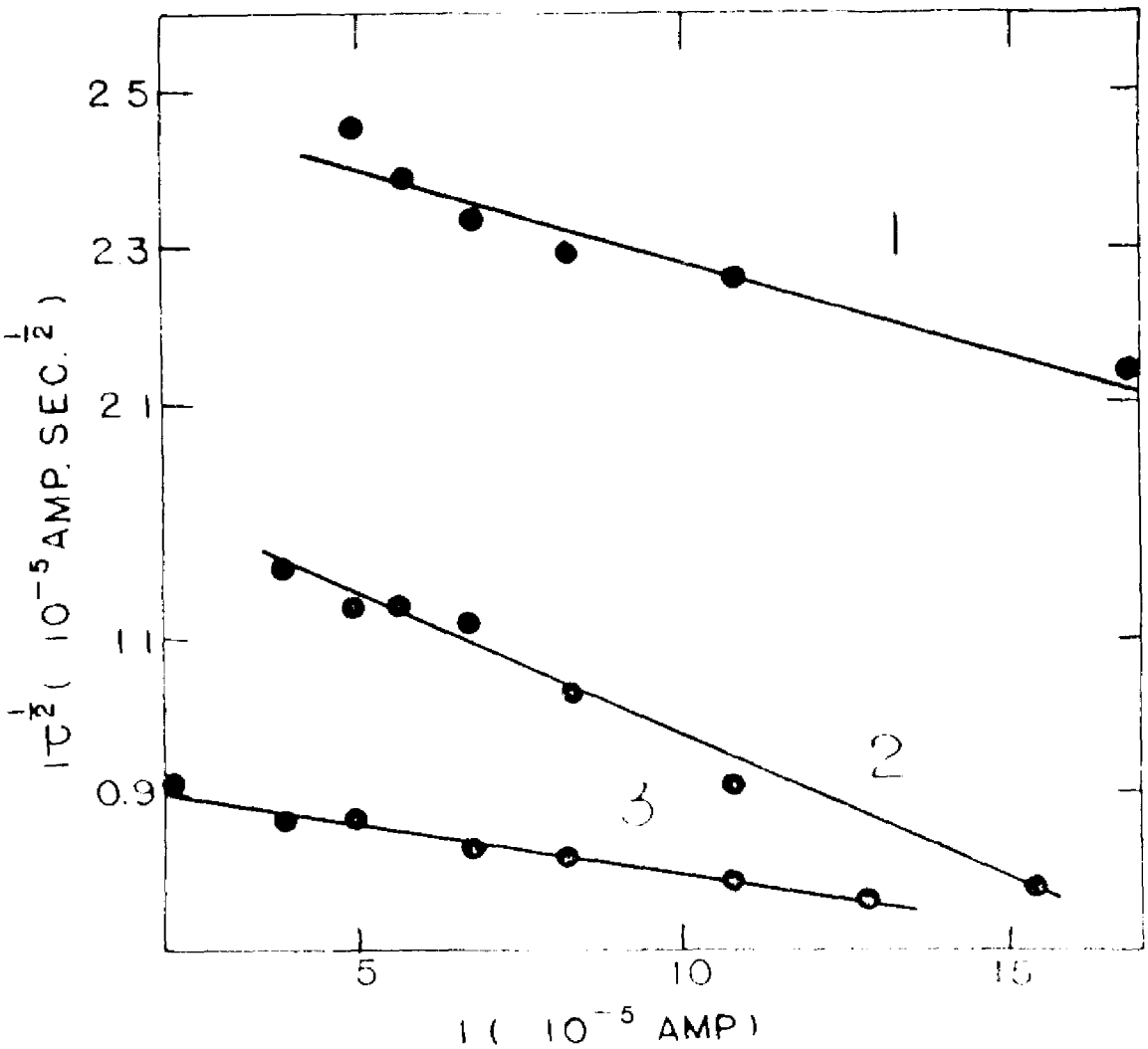

Figure 10

Variation of $i\tau^{1/2}$ with Current for Negative Complex Ions
(1) 1×10^{-3} M Cd^{++}, 1 M Potassium Iodide, 1 M Potassium Nitrate
(2) 2×10^{-3} M Cd^{++}, 0.5 M Disodium Tartrate, 1 M Sodium Nitrate, pH...
(3) 1×10^{-3} M Ni^{++}, 1 M Potassium Cyanide, 1 M Potassium Nitrate

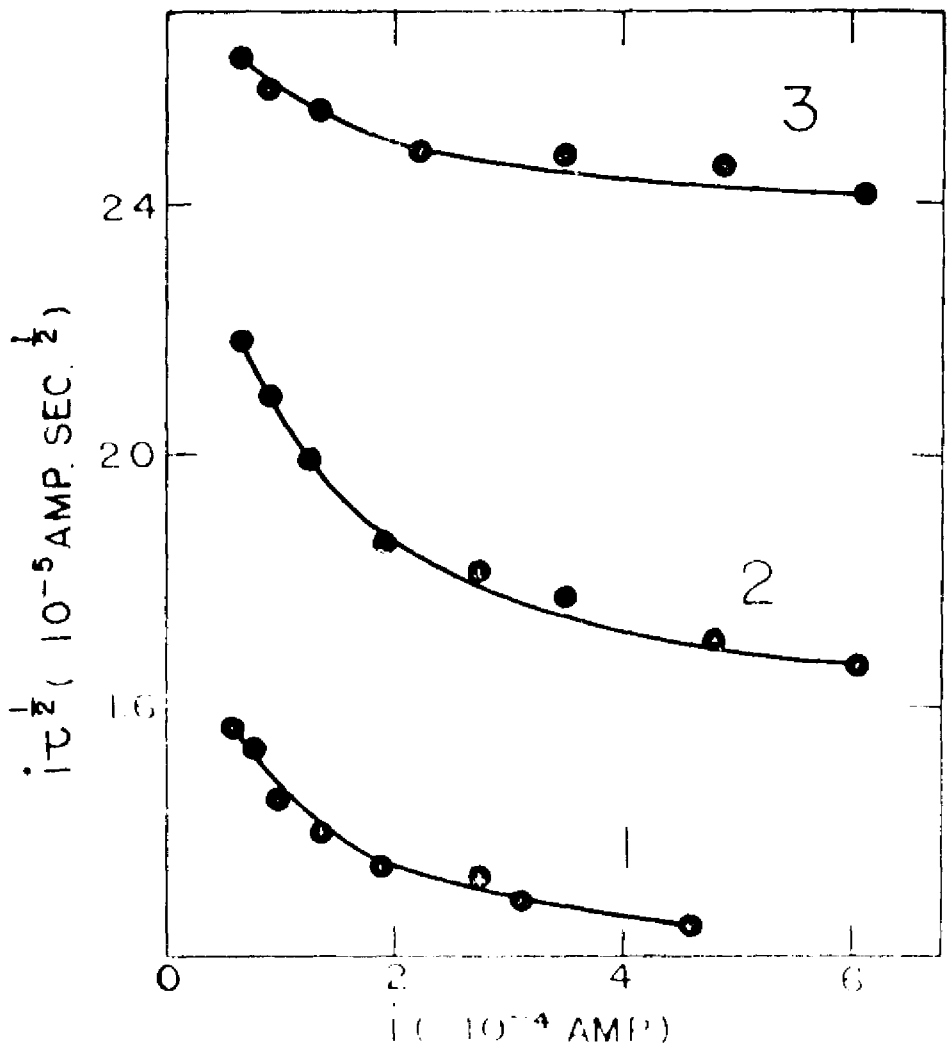

Figure 11

Variation of $i\tau^{1/2}$ with Current for Negative Complex Ions
(1) 5×10^{-3} M Fe^{+++}, 0.5 M Trisodium Citrate, pH 6.5
(2) 2×10^{-3} M Cu^{++}, 0.25 M Disodium Ethylenediaminetetraacetic Acid, 0.5 M Potassium Nitrate, pH=6
(3) 5×10^{-3} M Fe^{+++}, 0.5 M Potassium Oxalate, pH=4.9

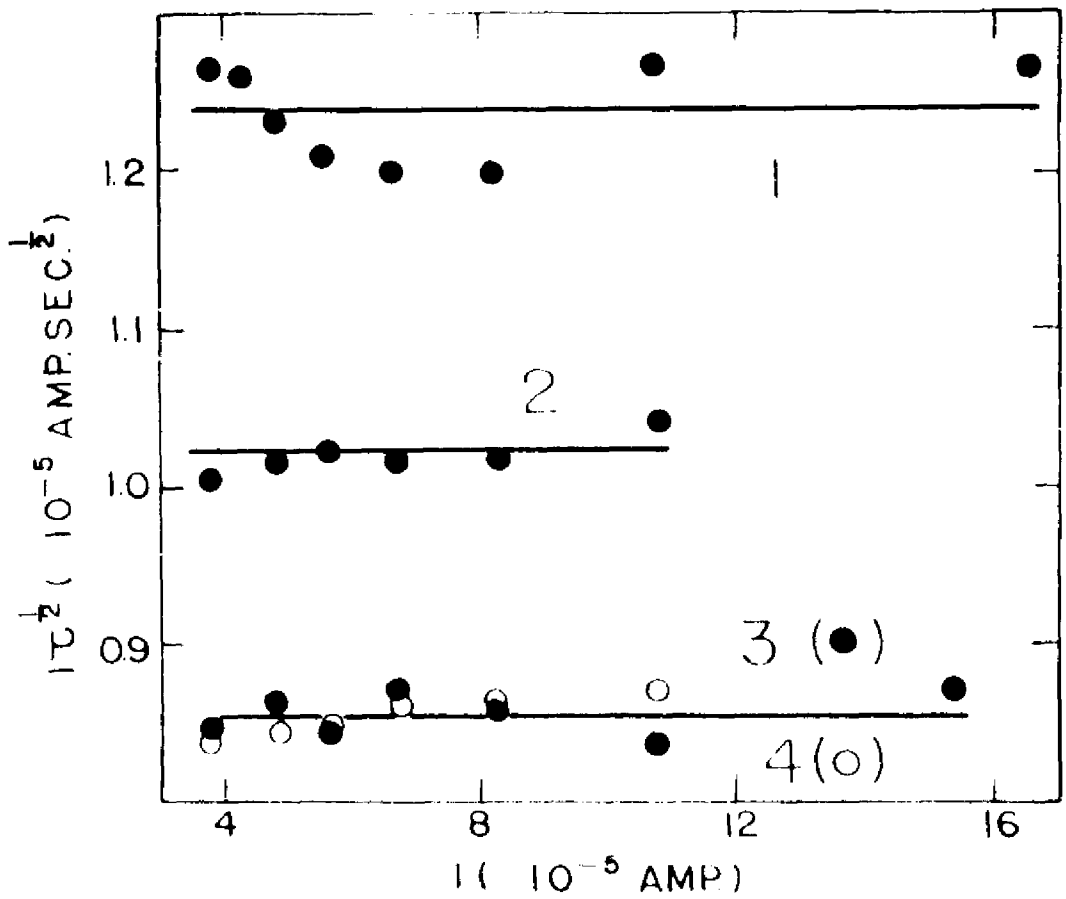

Figure 12

Variation of $i\tau^{1/2}$ with Current for Positive Complex Ions
(1) 1×10^{-3} M Zn^{++}, 2 M Ammonium Hydroxide, 1 M Ammonium Chloride
(2) 1×10^{-3} M Cd^{++}, 1 M Ammonium Hydroxide, 1 M Ammonium Chloride
(3) 1×10^{-3} M Zn^{++}, 0.1 M Ethylenediamine, 1 M Potassium Nitrate
(4) 1×10^{-3} M Cd^{++}, 0.1 M Ethylenediamine, 1 M Potassium Nitrate

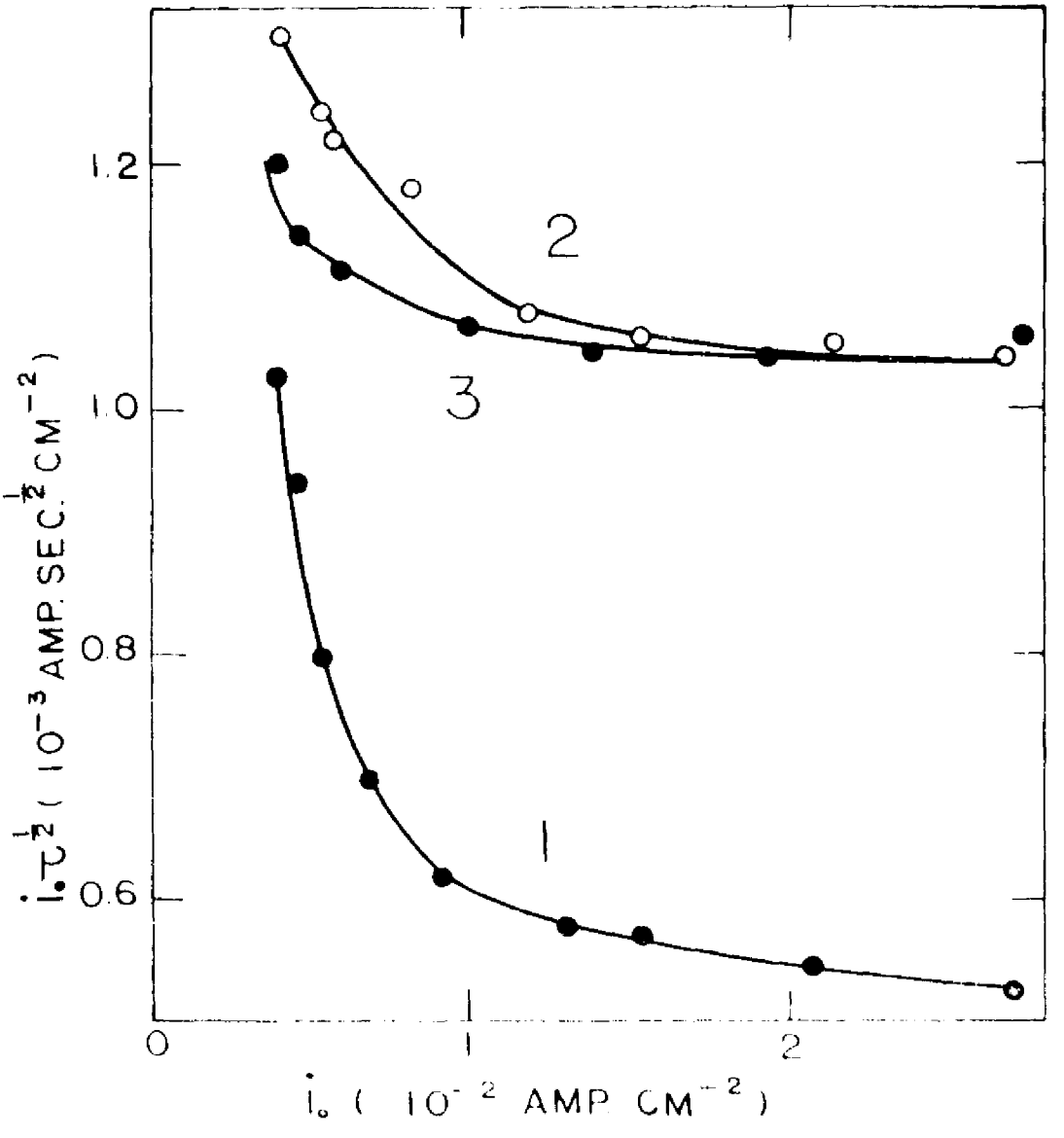

Figure 13

Effect of Concentration of the Complexing Agent on the Slope of the Plot $i_d\tau^{1/2}$ vs. i_d
5×10^{-3} M Cd^{++} in Trisodium Citrate
(1) 1.50 M Trisodium Citrate
(2) 0.50 M Trisodium Citrate
(3) 0.20 M Trisodium Citrate

preceding discharge the slope of $i_o\tau^{1/2}$ vs i_o should increase with the square root of the complexing agent concentration. Although the slope of $i_o\tau^{1/2}$ vs. i_o for small current densities increased with the concentration of the citrate ion, the square root dependence of the slope on concentration was not obtained. The explanation probably lies in the simultaneous occurence of the direct reduction of the complex. The dual mechanism of direct reduction and dissociation prior to reduction is, in principle, possible for all of these negative complexes. However, when the complexes are discharged in a range of potentials in which the electrode is very negative with respect to the solution, direct reduction is very slow. The direct reduction mechanism should become important for complexes which are discharged at the potentials at which the electrode has a positive charge with respect to solution. In the case of cadmium citrate the direct reduction probably takes place since the reduction potential of the complex is only 0.2 volt more negative than the potential of zero charge of mercury. Also, as shown by polarographic studies (26), the complex has only one negative charge. If one assumes the discharge by both mechanisms -- direct reduction and reduction preceded by dissociation -- it is easily seen that the slope of $i_o\tau^{1/2}$ vs. i_o should not necessarily be proportional to the square root of the complexing agent. The mathematical treatment for the dual mechanism has not been worked out because it is very involved (non-linear boundary condition).

The direct reduction mechanism should be particularly important for ferric oxalate and citrate complexes since these complexes are discharged at the potentials more positive than the potential of zero charge.

Gerischer (12) in his determination of the rate constants for the dissociation

$$Cd(CN)_4^{=} \rightleftharpoons Cd(CN)_3^{-} + CN^{-}$$

obtained a straight line for the plot $-\frac{d(i\tau^{\frac{1}{2}})}{di}$ vs. $\sqrt{[CN^-]}$ for six concentrations of CN^- (0.2 M to 1.2M) ion thus verifying the square root dependence predicted by the theory. In this case, the reduction potential is much more negative than the potential of zero charge and the direct reduction mechanism is unimportant.

Charge of Metallic Complex and Rate Constants for the Electrochemical Discharge Reaction

Further evidence of the effect of charge on the mechanism of discharge is obtained from the determination of the kinetic parameters for the electrode reaction for the different complexes of the same metal and ligand. Data for such a study are available for the cadmium cyanide complexes (14).

The kinetics of discharge of a metal ion with amalgam formation can be characterized by the exchange current density, which is

$$j_o = nFk_s\left(C^o_{M_i}\right)^{1-\alpha}\left(C^o_M\right)^{\alpha} \qquad (8\text{-}1)$$

where $C^o_{M_i}$ and C^o_M are the equilibrium concentrations of the species being discharged and metal M in mercury, respectively; α is the transfer coefficient and k_s the rate constant at the standard potential E^o. The parameters k_s and α characterize the electrode reaction. When the experimentally determined exchange current densities and the instability constants for the various complexes of a series are known, it is possible to calculate the rate constant k_s for the reduction of a specific complex species. The results of such calculations are given in Table III. The instability constants for the different cadmium cyanide complexes were given by Siekierski (35). The data of Table III indicate that the rate of the electrochemical reaction increases with increasing positive charge on the complex. However, it should be pointed out that in concentrated cyanide

TABLE [illegible]

RATES OF DISCHARGE OF CADMIUM CYANIDE COMPLEXES

ON CADMIUM AMALGAM AT 25° C

Reducible Species	E^{o} (volts)	k_s[1] (cm.sec^{-1})
Cd^{++}	-0.647	4.2×10^{-2}
$Cd(CN)_2$	-1.207	1.9×10^{-2}
$Cd(CN)_3^-$	-1.122	1.3×10^{-3}
$Cd(CN)_4^{--}$	-----	-----

[1]Calculated from the data of Gerischer [14] measurements made with the hanging amalgam drop.

solutions the concentration of the free Cd^{++} is extremely low thus the contribution of Cd^{++} ion to the exchange current density will be negligible. Gerischer (14) states that at low CN^- concentrations the reduction occurs through the neutral $Cd(CN)_2$ species, but at high concentrations of the complexing agent the reducible species is $Cd(CN)_3^-$ complex.

Conclusion

The following mechanism is proposed for the discharge of negatively charged metallic complexes. (1) Reduction occurs simultaneously (a) by the direct electrochemical reaction of the complex and (b) with chemical transformation $MX_p^{-q} \rightleftharpoons MX_{p-1}^{-(q-1)} + X^-$ prior to reduction. (2) The relative contribution of these two simultaneous processes varies with potential. Reduction with preceding chemical transformation is predominant at potentials markedly negative with respect to the point of zero charge. Conversely, direct reduction is predominant at potentials sufficiently positive with respect to the point of zero charge. There is a progressive transition from one extreme case to the other.

Complex ions with a positive charge which were studied are reduced directly.

APPENDIX

DERIVATION OF

DIFFUSION STRIPPING CURRENT OF EQUATION (2-3)

As stated in Chapter II, the derivation of the diffusion stripping current requires the solution of Fick's diffusion equation

$$\frac{\partial C_M}{\partial t} = D_M \frac{\partial^2 C_M}{\partial x^2} \qquad \text{(A-1)}$$

for the following initial and boundary conditions.

The initial condition is given by the relationship

$$C_M(x, 0) = \frac{i_p}{nFAD_M}\left[2\left(\frac{D_M\tau}{\pi}\right)^{1/2} \exp\left(-\frac{x^2}{4D_M\tau}\right) - x\,\mathrm{erfc}\left(\frac{x}{2D_M^{1/2}\tau^{1/2}}\right)\right] \qquad \text{(A-2)}$$

which can be conveniently written by the introduction of

$$\theta = \frac{i_p}{nFAD_M} \qquad \text{(A-3)}$$

The boundary conditions are

$$C_M(0, t) = 0 \quad \text{for} \quad t > 0 \qquad \text{(A-4)}$$

$$C_M(x, t) \longrightarrow 0 \quad \text{for} \quad x \longrightarrow \infty \quad \text{and} \quad t \geq 0 \qquad \text{(A-5)}$$

By taking the Laplace transform of equation (A-1) with respect to time one obtains the following ordinary differential equation (3, 4)

$$\frac{d^2\bar{C}_M(s, x)}{dx^2} - \frac{s}{D_M}\bar{C}_M(s, x) = -\frac{C_M(x, 0)}{D_M} \qquad \text{(A-6)}$$

where $C_M(x, 0)$ is given by (A-2). The solution of this equation is of the form

$$\bar{C}(s, x) = M\exp\left[-\left(\frac{s}{D_M}\right)^{1/2}x\right] + N\exp\left[\left(\frac{s}{D_M}\right)^{1/2}x\right] + \bar{C}_p(s, x) \qquad \text{(A-7)}$$

where M and N are integration constants and $\bar{C}_p(s,x)$ is a particular solution of equation (A-6). This particular solution is given by the relationship (36)

$$\bar{C}_p(s,x) = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} \frac{\Phi(p)}{\Psi(p)} \exp(px)\, dp \qquad \text{(A-8)}$$

where $i=(-1)^{1/2}$; γ is a positive constant, $\Phi(p)$ is the Laplace transform of the function $-C_M(x,0)/D_M$ with respect to x, (using p instead of s to avoid confusion with the previous transformation), and $\Psi(p)$ is the symbolic formulation of equation (A-6) (33). In the present case one has

$$\Psi(p) = p^2 - \frac{s}{D_m} \qquad \text{(A-9)}$$

The integral (A-8) in which $\Psi(p)$ is replaced by its value from (A-9) can be evaluated by application of the convolution theorem for the Laplace transform (36). Thus

$$\bar{C}_p(s,x) = \int_0^x f(\eta)\, g(x-\eta)\, d\eta \qquad \text{(A-10)}$$

in which η is an auxiliary variable and the functions f (x) and g (x) are defined as follows f (x) = $-C_M(x,0)/D_M$ and g (x) is such that the function $1/\Psi(p)$ [see (A-9)] is the Laplace transform of g (x). Hence (4)

$$g(x) = \frac{1}{s/(D_m)^{1/2}} \sinh\left[\left(\frac{s}{D_m}\right)^{1/2} x\right] \qquad \text{(A-11)}$$

In view of equations (A-10) (A-11) and the definition of the function f (x), the particular solution $\bar{C}_p(s,x)$ is

$$\bar{C}_p(s,x) = -\frac{\theta}{D_m^{1/2} s^{1/2}} \int_0^x \left[\frac{2 D_m^{1/2} \tau^{1/2}}{\pi^{1/2}} \exp\left(-\frac{\eta^2}{4 D_m \tau}\right) - \eta \operatorname{erfc} \frac{\eta}{2 D_m^{1/2} \tau^{1/2}}\right] \sinh\left[\frac{s^{1/2}}{D_m^{1/2}}(x-\eta)\right] d\eta \qquad \text{(A-12)}$$

or, in an abridged form

$$\bar{C}_p(s,x) = -\frac{\Theta}{D_m^{1/2} s^{1/2}} I_1 \qquad \text{(A-13)}$$

where I_1 corresponds to the integral of equation (A-12).

The integral I_1 is evaluated by successive integrations by parts. It is convenient to make the following substitutions

$$a = \frac{1}{2 D_m^{1/2} \tau^{1/2}} \qquad q = -\frac{s^{1/2}}{D_m^{1/2}} \qquad \text{(A-14)}$$

and to rewrite I_1

$$I_1 = \int_0^x \left[\frac{1}{\pi^{1/2} a} \exp(-a^2\eta^2) - \eta \operatorname{erfc}(a\eta)\right] \cdot \sinh\left[q(x-\eta)\right] d\eta \qquad \text{(A-15)}$$

In the first integration one sets

$$u = \frac{1}{\pi^{1/2} a} \exp(-a^2\eta^2) - \eta \operatorname{erfc}(a\eta) \qquad \text{(A-16)}$$

$$dv = \sinh\left[q(x-\eta)\right] d\eta \qquad \text{(A-17)}$$

After integration this leads to a second integral

$$I_2 = \int_0^x \operatorname{erfc}(a\eta) \cdot \cosh\left[q(x-\eta)\right] d\eta \qquad \text{(A-18)}$$

which is evaluated by setting $\operatorname{erfc}(a\eta)$ as u and the remaining terms as dv. The following third integral is obtained in this manner

$$I_3 = \int_0^x \exp(-a^2\eta^2) \cdot \sinh\left[q(x-\eta)\right] d\eta \qquad \text{(A-19)}$$

This integral is calculated by substituting for the hyperbolic sine the corresponding exponential functions.

One finally obtains for I_1

$$I_1 = -\frac{1}{q}\left[\frac{1}{\pi^{1/2} a} \exp(-a^2x^2) - x \operatorname{erfc}(ax)\right] + \frac{1}{q\pi^{1/2} a} \exp(qx) + \exp(-qx) - \frac{1}{q^2} \exp(qx) - \exp(-qx) + \frac{1}{2q^2} \exp\left(\frac{q^2}{4a^2} + qx\right) \operatorname{erf}\left(ax + \frac{q}{2a}\right)$$

$$- \frac{1}{2q^2} \exp\left(\frac{q^2}{4a^2} - qx\right) \operatorname{erf}\left(ax - \frac{q}{2a}\right) \qquad \text{(A-20)}$$

After some transformations one obtains for the complete solution of equation (A-6) the following expression

$$\bar{C}(s,x) = M' \exp(-qx) + N' \exp(qx)$$
$$+ \frac{\theta}{s}\left[\frac{1}{\pi^{1/2}a} \exp(-a^2x^2) - x \operatorname{erfc}(ax)\right]$$
$$+ \frac{\theta D_m^{1/2}}{2 s^{3/2}} \exp\left(\frac{q^2}{4a^2} + qx\right) \operatorname{erfc}\left(ax + \frac{q}{2a}\right)$$
$$+ \frac{\theta D_m^{1/2}}{2 s^{3/2}} \exp\left(\frac{q^2}{4a^2} - qx\right) \operatorname{erf}\left(ax - \frac{q}{2a}\right) \qquad \text{(A-21)}$$

The integration constants M' and N' in equation (A-21) are different from the constants M and N of equation (A-7), because terms in exp (-qx) and exp (qx) from the complementary and particular solution have been combined. It is necessary to set N' = 0 since $\bar{C}$ (s, x) cannot increase indefinitely with x. M' is obtained from the transform of the boundary condition (A-4). Thus $\bar{C}_M$ (s, 0) = 0 and

$$M' = -\frac{\theta}{s}\frac{1}{\pi^{1/2}a} - \frac{\theta D_m^{1/2}}{2 s^{3/2}} \exp\left(\frac{q^2}{4a^2}\right) \operatorname{erfc}\left(\frac{q}{2a}\right)$$
$$+ \frac{\theta D_m^{1/2}}{2 s^{3/2}} \exp\left(\frac{q^2}{4a^2}\right) \operatorname{erf}\left(\frac{q}{2a}\right) \qquad \text{(A-22)}$$

Since we are interested in the flux at x = C, rather than the concentration, we can differentiate $\bar{C}$ (s, x) with respect to x and set x = 0 in the resulting equation. One then obtains

$$\left[\frac{d\bar{C}_m(s,x)}{dx}\right]_{x=0} = \frac{\theta}{s}\left(\frac{q}{\pi^{1/2}a} - 1\right)$$
$$+ \frac{\theta D_m^{1/2}}{s^{3/2}} q \exp\left(\frac{q^2}{4a^2}\right) \operatorname{erfc}\left(\frac{q}{2a}\right) \qquad \text{(A-23)}$$

Upon introduction of the values of a and q there follows

$$\left[\frac{d\bar{C}_M(s,x)}{dx}\right]_{x=0} = \Theta\left[\frac{2\tau^{1/2}}{\pi^{1/2}}\,\frac{1}{s^{1/2}} - \frac{1}{s}\cdot\right.$$

$$\left. + \frac{1}{s^{1/2}}\cdot\frac{1}{s^{1/2}}\,\exp(s\tau)\,\mathrm{erfc}(s\tau)^{1/2}\right] \qquad \text{(A-24)}$$

The inverse transforms for the first two terms are (4)

$$L^{-1}\left(\frac{1}{s^{1/2}}\right) = \frac{1}{\pi^{1/2}\,t^{1/2}}$$

$$L^{-1}\left(\frac{1}{s}\right) = 1 \qquad \text{(A-25)}$$

The transform of the third term can be evaluated by application of the convolution theorem (4). Since

$$L^{-1}\left[\frac{1}{s^{1/2}}\exp(s\tau)\,\mathrm{erfc}(s\tau)^{1/2}\right] = \frac{1}{\pi^{1/2}(\tau+t)^{1/2}}$$

Therefore

$$L^{-1}\left[\frac{1}{s^{1/2}}\cdot\frac{1}{s^{1/2}}\exp(s\tau)\,\mathrm{erfc}(s\tau)^{1/2}\right]$$

$$= \frac{1}{\pi}\int_0^t \frac{dz}{z^{1/2}(\tau+t-z)^{1/2}} = \frac{2}{\pi}\sin^{-1}\frac{t^{1/2}}{(\tau+t)^{1/2}} \qquad \text{(A-26)}$$

z being an auxiliary variable. If one uses the trigonometric identity (32)

$$\sin^{-1}y = \frac{1}{4}\pi + \frac{1}{2}\sin^{-1}(2y^2-1)$$

one can write (A-26) as follows

$$L^{-1}\left[\frac{1}{s^{1/2}}\cdot\frac{1}{s^{1/2}}\exp(s\tau)\,\mathrm{erfc}(s\tau)^{1/2}\right]$$

$$= \frac{1}{2} - \frac{1}{\pi}\sin^{-1}\frac{\tau-t}{\tau+t} \qquad \text{(A-27)}$$

Thus one finally obtains the flux as

$$\left[\frac{\partial C_M(x,t)}{\partial x}\right]_{x=0} = \theta\left[\frac{2}{\pi}\left(\frac{\tau}{t}\right)^{1/2} - \frac{1}{2} - \frac{1}{\pi}\sin^{-1}\frac{\tau - t}{\tau + t}\right] \qquad \text{(A-28)}$$

Since

$$i_{s,d} = -nFAD_M\left[\frac{\partial C_M(x,t)}{\partial x}\right]_{x=0} \qquad \text{(A-29)}$$

where the anodic current is negative according to polarographic convention and θ is given by equation (A-3), one obtains for the diffusion stripping current the following equation given in Chapter II as equation (2-3)

$$-\frac{i_{s,d}}{i_p} = \frac{2}{\pi}\left(\frac{\tau}{t}\right)^{1/2} - \frac{1}{2} - \frac{1}{\pi}\sin^{-1}\frac{\tau - t}{\tau + t} \qquad \text{(A-30)}$$

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Gleb Mamantov was born April 10, 1931, in Karsava, Latvia. He received his elementary education in the Karsava public school from which he graduated in 1944. He went the same year to Germany where he lived in the Displaced Persons Camp Kleinkotz. In 1945 he entered Ausma High School and graduated from it in 1949.

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Title of Thesis:

Approved:

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Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination: